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Analysis of Laser-Enhanced Adsorption/Desorption
Processes on Semiconductor Surfaces via
Electronic Surface State Excitation

by

William C. Murphy, A. C. Beri, Thomas F. George and Jui-teng Lin

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ANALYSIS OF LASER-ENHANCED ADSORPTION/DESORPTION PROCESSES ON SEMICONDUCTOR SURFACES VIA ELECTRONIC SURFACE STATE EXCITATION

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ABSTRACT

Electronic surface states in semiconductors often lie between the valence and conduction bands and give rise to charge densities confined to the surface region. Laser radiation of frequency less than the energy gap can excite electrons from delocalized valence band states to these localized surface states leading to large changes in the charge distribution at the surface. Selective enhancement of adsorption/desorption processes involving ionic or polar adspecies can result from such a charge redistribution. Using a one-dimensional model for silicon, the cross-section for the laser-induced electronic transition to surface states is shown to be large. The interaction energy of an adspecies with the surface changes significantly with direct excitation of surface states in a semiconductor. For a one-dimensional metal, however, direct transitions between bulk and surface states are not allowed, but phonon-mediated transitions coupled with laser radiation lead to substantial charge transfer as for semiconductors.

INTRODUCTION

Much effort has been devoted to the study of the effects of laser radiation on the phonons in solid surfaces. Both theoretical [1] and experimental [2] works have relied on the laser to excite these vibrational modes of the system in order to enhance surface processes.

On the other hand, photo-induced surface reactions can occur through electronic excitation. Synchrotron radiation studies [3] on metal surfaces have shown induced desorption due to the shift of electronic charge in the surface region [4].

For a semiconductor, states with charge localized in the surface region exist in addition to the bulk conduction and valence bands states [5]. In the following, we will demonstrate the use of a laser for exciting charge into these surface states and discuss the effect on surface processes.

For a truncated one-dimensional chain of length L and lattice constant a , the solutions of the Schrödinger equation can be obtained within the nearly-free-electron approximation [5]. The energy for the bulk electronic states is

$$E_k = \frac{1}{4}([k^2 + (k-g)^2] \pm \sqrt{[k^2 - (k-g)^2]^2 + 4E_g^2}) \quad (1)$$

where k is the wavenumber of the electron, $g = 2\pi/a$ is the reciprocal lattice vector and E_g is the band gap energy. The results for the valence band (negative branch) and conduction band (positive branch) are illustrated in figure 1. The wavefunctions are constructed from sums of plane waves [6]. For

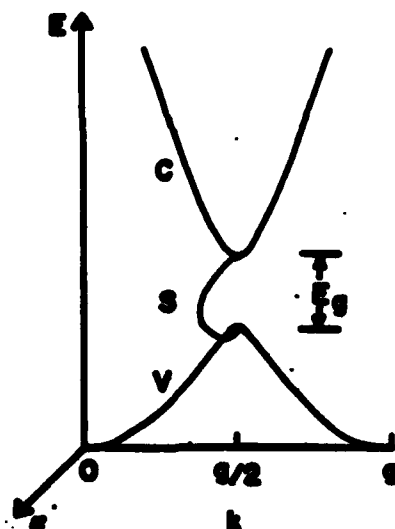


Figure 1. Dispersion relationship in complex crystal momentum space ($k+ik$) for a finite linear chain. The valence, surface and conduction bands are labeled V, S and C, respectively.

example, at the top of the valence band we have

$$\psi_k(z) = \frac{2}{L^{1/2}} \sin[(g/2)(z-a/2) + \theta] \quad (2)$$

for inside the chain and

$$\psi_k(z) = \frac{2}{L^{1/2}} \sin \theta e^{-q(z-\frac{a}{2})} \quad (3)$$

for outside the chain. The phase factor, θ , is determined by the continuity condition and $q = (2W-k^2)^{1/2}$, where W is the work function [6].

Since we have a truncated chain, in addition to the above solutions of the Schrödinger equation, we can have solutions with complex crystal momentum [5].

$$k = g/2 + i\kappa. \quad (4)$$

Inserting this into our energy, equation (1), we obtain

$$E_\kappa = \frac{1}{2} \left\{ \left(\frac{g}{2} \right)^2 - \kappa^2 \pm \sqrt{\left(\frac{g}{2} \right)^2 - \kappa^2} \right\}. \quad (5)$$

Likewise using equation (2), we obtain the wavefunction

$$\psi_\kappa(z) = C_g \sin\left[\left(\frac{g}{2}\right)\left(z-\frac{a}{2}\right) + \theta\right] e^{-\kappa(z-\frac{a}{2})} \quad (6)$$

where C_g is a normalization constant. The external wavefunction will have the same form as equation (3). Here we have disregarded the contribution to the wavefunction at the far surface ($z = a/2-L$). The energy, equation (5), is also illustrated in figure 1 by the band labeled S. These are surface states since the charge density associated with them is localized in the surface region due to the exponential factor in equation (6). The bulk states, equation (2), however, have charge more or less uniformly distributed throughout the system.

Consequently, if we excite electrons from the valence band to the surface band, we can transfer charge from the bulk of our crystal to the surface. The resultant Coulombic effect could have significant effect on surface processes. To explore this concept, we first wish to see how well laser radiation can excite charge into the surface states.

SURFACE STATE EXCITATION

Laser induced transitions to the surface states will be governed by the integral

$$H_{\kappa k}(t) = \langle \kappa | \vec{A} \cdot \vec{p} | k \rangle, \quad (7)$$

where \vec{A} is the vector potential of the laser radiation and \vec{p} is the momentum operator of the electron. If we use a laser that is polarized parallel to the chain and exploit the periodicity of the functions contained in our wave-function [6], we obtain

$$H_{\kappa k}(t) = -i \left(\frac{2\pi I}{137} \right)^{1/2} \frac{e^{-i\omega t}}{\omega} S \langle \kappa | \frac{d}{dx} | k \rangle_0, \quad (8)$$

where I is the intensity of the laser, ω is the frequency and the subscript zero indicates integration over the first unit cell. The sum, S , is given by

$$S = \sum_{l=0}^{N-1} e^{i(g/2-k)la} e^{\kappa la}, \quad (9)$$

where N is the number of atoms in our chain. To obtain the transition probability, we would take the square modulus of equation (8). If we assume that N is very large [6], the sum squared can be approximated by

$$|S|^2 \approx \frac{2\pi}{a} \frac{\delta(k-g/2)}{1-e^{2\kappa a}}, \quad (10)$$

where $\delta(k-g/2)$ is the Dirac delta function. Consequently, the transition from the bulk to a surface state is only permitted if the real part of the crystal momentum remains unchanged. This relationship is not too surprising since it is an exact restriction of laser-induced transitions between bulk bands [7]. Furthermore, for our model, it confines us to the top of the valence band, where the density of states is a maximum (infinite) and the laser frequency needed for a transition is a minimum.

To first order, the transition rate from the valence band to the surface band is

$$T = \left(\frac{2\pi}{t} \right) \sum_{\kappa} \sum_k \int_0^t | \int_0^t dt' H_{\kappa k}(t') e^{i\omega_{\kappa k} t'} |^2, \quad (11)$$

where $\omega_{\kappa k} = E_{\kappa} - E_k$. Using equations (8) and (10) in this expression, after evaluating the sums and time integral the transition rate becomes

$$T = \frac{8\pi}{137} \frac{I g_L^2}{E_g^2} \frac{|\langle \kappa | \frac{d}{dx} | g/2 \rangle_0|^2}{1-e^{2\kappa a}} \left| \frac{dk}{dE_{\kappa}} \right|, \quad (12)$$

where κ now refers to the state obeying the resonance condition

$$\omega = \frac{1}{2} [E_g - k^2 \pm (E_g^2 - g^2 \kappa^2)^{1/2}]. \quad (13)$$

The integral over the wavefunctions and the energy derivative can be readily evaluated [6]. Finally, we obtain the cross section, σ , from the relationship,

$$\sigma \approx \frac{\omega T}{I}. \quad (14)$$

Although the complete expression for σ is quite complicated [6], we can make some simple observations.

If the exciting laser radiation is at a frequency near $0.5 E_g$, the energy derivative will vanish and

$$\sigma_{\omega=0.5 E_g} = 0. \quad (15)$$

This is exactly what one would expect since this mid-gap energy is a branch point at which no surface state exists.

If the laser radiation is near a frequency 0 or E_g , the cross-section becomes

$$\sigma_{\omega \rightarrow 0, E_g} \sim \left| \frac{1}{\kappa} \right|. \quad (16)$$

At both extremes κ goes to zero and σ diverges. This occurs because at the surface band edges the charge associated with the surface states becomes more and more delocalized throughout the lattice, until at $\kappa = 0$ the charge is completely delocalized. At this point the surface states become bulk states, and instead of cross-sections, one should consider absorption coefficients.

Figure 2 depicts the behavior of the cross-section over the entire frequency range. The values for the lattice constant, $a = 2.35 \text{ \AA}$, and the energy gap, $E_g = 1.17 \text{ eV}$, are typical of silicon [8].

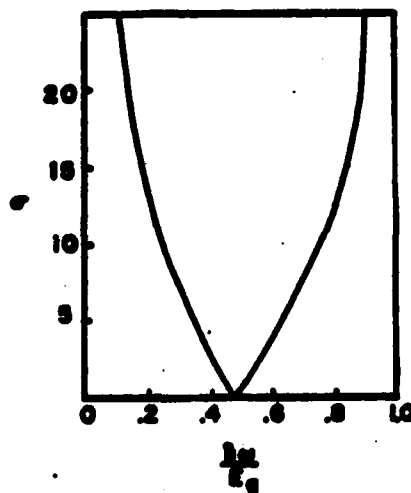


Figure 2. Absorption cross-section for surface states, σ , in \AA^2 versus the frequency of the exciting laser radiation.

To illustrate what laser intensity is required for a certain absorption rate, we consider exciting a surface state at $0.4 E_g$. This corresponds to a laser frequency of about 10^{15} Hz which falls in the infrared. From figure 2, the cross-section is about 3 \AA^2 . If we assume our laser intensity is 1 W/cm^2 , the transition rate is about 4×10^{-5} photons absorbed per second. Since an electron is excited for each photon absorbed and the effective charge depth for the surface state is about 8 atomic layers, the transition rate is about 5×10^{-6} electrons per surface atom per second. To obtain the number of transitions per unit surface area, we divide by the surface area of the end atom, whereby we obtain 10^{10} photons absorbed per cm^2 per second. This value is quite large considering the low power of the laser. Consequently, using such a laser can lead to appreciable charge excitation in the surface region.

Since the charge depth increases as we move away from the mid-gap region, we wish to excite surface states near $0.5 E_g$ to obtain the greatest effect on surface charge. From figure 2, we see that in this region the cross-section is quite substantial. Consequently, we would expect a laser tuned to a frequency near $0.5 E_g$ to be an effective controller of surface charge.

ADSPECIES-SURFACE INTERACTION

To examine the effect of this surface charge on adspecies, we must first determine the charge profile in the surface region. For the unexcited system, the electron density is

$$n_0(z) = \frac{\pi}{2} \int_0^{k_F} dk (E_F - E_k) |\psi_k(z)|^2 \quad (17)$$

where the subscript 0 indicates ground state and E_F is the Fermi energy with crystal momentum k_F . If the semiconductor is now exposed to a laser with an energy less than the energy gap, an electron will be excited from state $k = g/2$ to a surface state indicated by κ . The new density will be the sum of the ground state density and the surface state density less the change associated with the excited bulk state. However, the bulk state is delocalized throughout the system and its effect on the density will be negligible. Therefore, the excited system will have a density

$$n(z) = n_0(z) + |\psi_\kappa(z)|^2. \quad (18)$$

We have evaluated the densities for silicon and the results are depicted in figure 3. The solid line is the ground state charge density. The oscillations of the charge as one goes into the bulk of the crystal is due to the concentration of charge around the ions. The dashed line represents the density for the system with the excited surface state of $\kappa = 0.5 E_g/g$ in the lower branch. As can be seen by this plot, the charge in the excited surface state produces a total electronic charge in the surface region that is twice as great as the bulk average. If one excites surface states closer to the branch point near the gap center, the charge concentration in the first few layers of the surface will increase up to about thrice the average density.

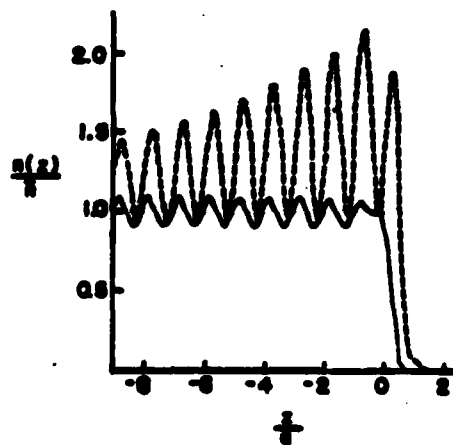


Figure 3. Electron density distribution at the surface. The solid line represents the ground electronic state, and the dashed line represents the system with the excited surface state $\kappa = 0.5 E_g/g$ in the lower branch.

If a charged adspecies is above the surface, this excess charge in the surface region can produce a marked effect on the adspecies surface interaction. This interaction can be written classically as

$$U(z_I) = - \int d\vec{r} n(z) v(r), \quad (19)$$

where $v(r)$ is the electron-ion potential of the adspecies at z_I . We have assumed that the charge density is uniform in the x and y directions. If we take $v(r)$ to be Coulombic with Thomas-Fermi screening [9], we can readily evaluate the integrals over x and y to obtain

$$U(z_I) = - \frac{2\pi Z}{\lambda} \int_{-\infty}^{\infty} dz n(z) e^{-\lambda |z - z_I|}, \quad (20)$$

where λ is the Thomas-Fermi screening parameter:

$$\lambda^2 = \frac{6\pi n}{E_F}. \quad (21)$$

Using our density expression, equation (18), we obtain

$$^s U(z_I) = \frac{2\pi Z}{\lambda} \int_{-\infty}^{\infty} dz |\psi_k(z)|^2 e^{-\lambda |z - z_I|}. \quad (22)$$

Since we are not concerned with the interaction of adspecies with the semiconductor in the ground state, we only consider the surface contribution to the potential (superscript s) in equation (22). If we now insert the expression for the surface wavefunction in equation (22), we will obtain

$$\frac{^s U(z_I)}{Z} = e^{-\lambda z_I} A(\kappa) - e^{-2\lambda z_I} B(\kappa) \quad (23)$$

where the coefficients $A(\kappa)$ and $B(\kappa)$ are given elsewhere [10]. The potential in equation (23) is exponentially damped as one moves away from the surface. In the vicinity of the surface the effect on the total potential can be quite

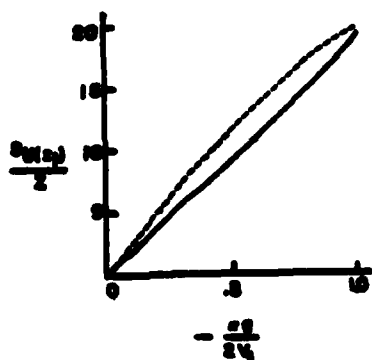


Figure 4. The magnitude of the surface interaction potential (in millihartrees) at a distance $z_I = a$ for the system with various excited surface states. The solid line represents surface states in the lower energy branch; the dashed line, the upper energy branch.

substantial. To illustrate this for various surface states, we have plotted the change in potential at $x_1 = a$ for all surface states in figure 4. The upper branch states are at a higher energy than the lower branch states. Therefore, the exponential tail of the charge density and, subsequently, the interaction is slightly greater.

Our contention that lasers can control surface charge density in semiconductors and, subsequently, enhance surface processes has been confirmed. Since metals also play an important role in catalysis, the effect of lasers on metal surfaces will also be examined via a simple model.

ELECTRON-PHONON COUPLING

If we model a metal as a truncated one-dimensional chain, we will obtain expressions for the bulk and surface wavefunctions and their associated energies which are the same in form as those for the one-dimensional semiconductor. However, whereas the lower band in a semiconductor is completely filled (see figure 1), in a metal this band is only partially filled. For example, in the case of sodium [8], the top of the lower band lies at 3.8 eV but the band is only occupied up to 3.1 eV in the ground state.

If we shine a laser on our metal, we cannot directly excite electrons from the bulk to the surface. This is due to our selection rule [see equation (10)] which says that we can only excite bulk states with $k = g/2$. In a metal, there are no occupied bulk states with real momentum at or near this crystal momentum. To overcome this problem, the electrons can be excited to the $k = g/2$ state with the phonons of the crystal before excitation into the surface states by the laser photons. Thus photons would supply the energy needed for the transition and phonons would supply the needed crystal momentum. Figure 5 illustrates the bands in a metal and the suggested pathway for exciting surface states.

Since the first-order transition probability will vanish since neither crystal momentum nor energy are conserved, we can write the transition probability of state k'' to k via intermediate state k' as

$$M = 2\pi\delta(\omega_{kk''} - \omega_f - \omega_p) \left(\sum_{k'} \frac{E_{kk'} E_{k'k''}}{\omega_{k'k''} - \omega_p} \right)^2 \quad (24)$$

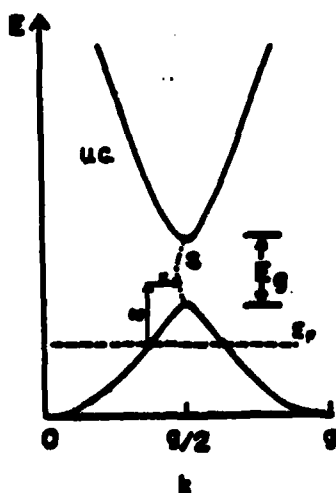


Figure 5. Dispersion relation for a metal and an excitation pathway to the surface states(s). The vertical arrow represents a photon of frequency ω ; the horizontal arrow, a phonon of momentum K . UC is an upper conduction band.

where the super- and subscripts f and p refer to the laser field and the phonons respectively. The matrix element $H_{kk'}^f$, is equivalent to equation (7) with the time exponential factored out. The phonon matrix element can be written [7],

$$H_{k'k}^p = -i \left(\frac{1}{NM} \right)^{1/2} \frac{Kv(K)}{2\omega_p} [a(K) + a^\dagger(K)] \quad (25)$$

where M is the mass of the lattice atom, $a(K)$ and $a^\dagger(K)$ are the annihilation and creation operators of the phonon, $v(K)$ is the form factor, and the crystal momentum of the phonon, K , must equal $k'-k$.

If we insert equations (7) and (25) into equation (24) and average over the phonon number states, $|n(K)\rangle$, we obtain the transition probability. If we now sum over all initial and final states, we will obtain the second-order transition rate

$$T = \left(\frac{L}{NM\hbar} \right) \int dk'' \frac{K^2 v(K)^2 [2n(K)+1]}{2\omega_p (\omega_{g/2,k''} - \omega_p)^2} T^{(1)}(k, g/2), \quad (26)$$

where $K = g/2 - k''$. $T^{(1)}(k, g/2)$ is the first-order transition rate between bulk state $g/2$ and surface state k induced by the laser field and is given by equation (12). We can convert this expression into an integral over energy. If we then assume a thermal distribution of phonons and electrons, we need only consider the integral within an interval $k_B T_L$ around the Fermi energy where T_L is the lattice temperature. At room temperature, this interval is small and the integrand can be considered a constant:

$$T = \left(\frac{ak_B T_L}{2\pi\hbar} \right) \left(\frac{k_F}{2E_F} \right) \frac{K^2 v(K)^2 [2n(K)+1]}{\omega_p (\omega_{g/2,k_F} - \omega_p)^2} T^{(1)}(k, g/2) \quad (27)$$

where $K = g/2 - k_F$.

For sodium we can readily evaluate equation (26):

$$T = 2.38 \times 10^{-4} T^{(1)}(k, g/2). \quad (28)$$

Since the various physical constants for sodium are not significantly different from those of silicon, we would expect the first-order rates to be roughly comparable. From the previous section, we saw that a significant photon absorption in silicon could be induced with a low power laser (1 to 10 W/cm²). Therefore, we would expect to produce a similar effect in sodium with a moderate power laser (10 to 100 kW/cm²). Consequently, as with semiconductors, we would expect a laser to act as an efficient controller of surface charge in a metal. Subsequent interactions would likewise be effected.

CONCLUSION

Using a laser to localize electronic charge in the surface region of a semiconductor or a metal can produce an appreciable effect on adspecies-surface interaction. For a negatively charged adspecies, desorption can be induced; if positively charged, adsorption is enhanced. In a more realistic model with both occupied and empty surface states, the laser could excite holes as well as

electrons and thus selectively enhance adsorption or desorption for the same charged adspecies.

Of course, this same formalism would apply to a polar adspecies. The positive end of a molecule would be attracted to a negatively charged surface. Thus, in addition to enhancing adsorption or desorption, the laser will cause the adspecies to line up in a desired orientation.

Furthermore, since the charge distribution of an adspecies is a function of its electronic state, our laser controlled surface could select the desired state. Finally, once molecules are adsorbed on the surface, new energy bands could be introduced through which the laser could enhance surface processes. To improve our understanding of the adspecies-surface system, the dielectric screening problem would have to be addressed in more detail.

Because the concentration of charge is so large in the surface region, it is conceivable that a lattice rearrangement could be induced in the surface area. Such an effect could lower the charge in the surface. On the other hand, the new surface states would probably be more stable and, subsequently, have a larger lifetime. To study these effects, a self-consistent-field calculation would have to be performed.

The major limitation of the above model, however, is its one-dimensionality. The three-dimensional interaction potential may be quite complex depending not only on the distance from the surface but also on the position of the adspecies with respect to the plane of the surface. Finally, in a real metal or semiconductor, the surface states are not necessarily confined to the gap between the valence and conduction bands.

Nonetheless, we have clearly demonstrated that lasers can be used to control surface charge in both metals and semiconductors. Such charge, in turn, can lead to enhanced surface processes. The effects on these processes of adspecies-surface dynamics and higher dimensions are the subject of continuing research.

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